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# 1-Butyl-2,3,3-trimethylindol-1-ium iodide

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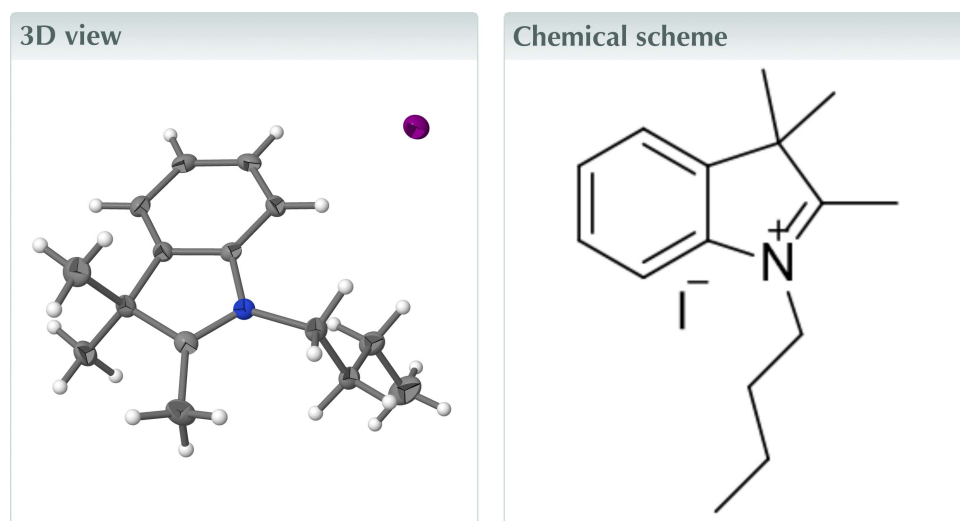
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Keywords: crystal structure; indole; cyanine precursor.

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Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

In the title molecular salt,  $C_{15}H_{22}N^+ \cdot I^-$ , the fused-ring system is slightly puckered [dihedral angle between the five- and six-membered rings =  $3.43(8)^\circ$ ]. In the crystal, very weak  $C-H \cdots I$  interactions link the cations to the anions. Photophysical data for the title salt in different solvents are presented.

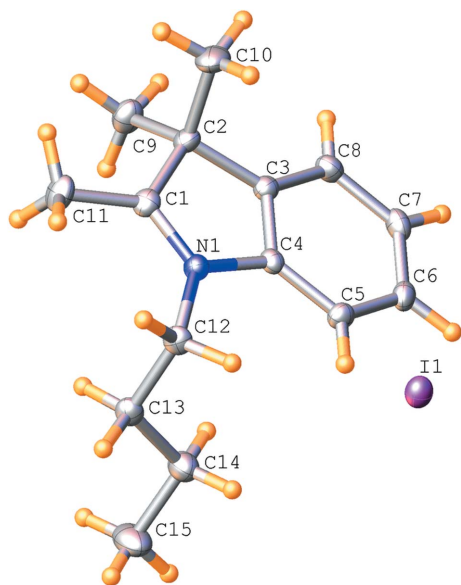


## Structure description

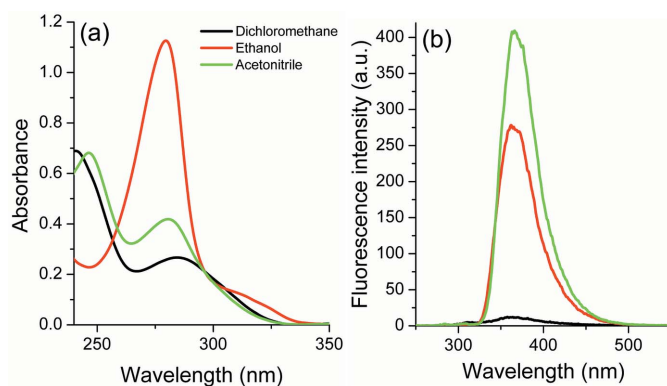
Recent studies have shown the importance of the indole nucleus with respect to its anticancer activities (Singh *et al.*, 2010; Shaveta, 2014) and in its biological applications as biosensors (Saikiran *et al.*, 2017; Guo *et al.*, 2015). As part of our studies of indole derivatives, we report here the crystal structure and optical properties of the title salt,  $C_{15}H_{22}N^+ \cdot I^-$ , bearing a quaternized indolic N atom with a butyl side chain.

The indole ring system (Fig. 1) is slightly puckered [dihedral angle between the rings =  $3.43(8)^\circ$ ]. The key torsion angles of the butyl side chain are  $N1-C12-C13-C14 = 76.14(18)^\circ$  and  $C12-C13-C14-C15 = 176.26(16)^\circ$ . In the crystal, there are possibly some very weak  $C-H \cdots I$  interactions (Table 1). Given that the van der Waals separation of H and I is 3.18 Å, some of these may barely qualify as directional bonds.

The absorption and emission spectra of the title compound are shown in Fig. 2. The relevant data from UV-Vis absorption spectroscopy in different solvents are presented in Table 2. The compound presents absorption maxima located between 279 and 285 nm related to allowed  $^1\pi\pi^*$  electronic transitions. The fluorescence emission spectra were obtained by exciting the compounds at the absorption maxima wavelength. The title compound shows emission in the UV-A region ( $\sim 365$  nm), with a small solvatochromic effect and a Stokes shift higher than  $7500\text{ cm}^{-1}$ .



**Figure 1**  
The molecular structure of the title compound, with displacement ellipsoids shown at the 50% probability level.



**Figure 2**  
UV-Vis absorption (a) and fluorescence emission (b) spectra in solution ( $10^{-5}$  M).

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C5-H5\cdots I1$	0.95	3.18	3.899 (2)	134
$C12-H12A\cdots I1^i$	0.99	3.29	4.186 (3)	151
$C12-H12B\cdots I1$	0.99	3.28	4.249 (3)	167
$C13-H13B\cdots I1^{ii}$	0.99	3.24	4.172 (3)	158

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

**Table 2**  
Relevant photophysical data of the UV-Vis absorption and fluorescence emission spectroscopy, where  $\lambda_{\text{ABS}}$  and  $\lambda_{\text{em}}$  are the absorption and emission maxima, respectively (nm),  $\epsilon$  is the molar absorptivity coefficient ( $\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and SS is the Stokes shift ( $\text{cm}^{-1}$ ).

Solvent	$\lambda_{\text{ABS}}$	$\epsilon$	$\lambda_{\text{em}}$	SS
Dichloromethane	285	0.79	363	7540
Ethanol	279	2.70	367	8594
Acetonitrile	281	0.89	370	8560

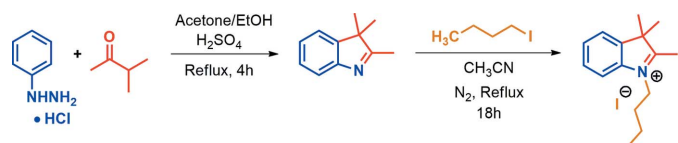
**Table 3**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{15}\text{H}_{22}\text{N}^+\text{I}^-$
$M_r$	343.23
Crystal system, space group	Orthorhombic, $Pbca$
Temperature (K)	150
$a, b, c$ ( $\text{\AA}$ )	15.631 (12), 11.614 (8), 16.976 (11)
$V$ ( $\text{\AA}^3$ )	3082 (4)
$Z$	8
Radiation type	Mo $K\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	2.06
Crystal size (mm)	$0.37 \times 0.10 \times 0.09$
Data collection	
Diffractometer	Bruker APEX CCD detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2015)
$T_{\text{min}}, T_{\text{max}}$	0.637, 0.746
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	41973, 3784, 3166
$R_{\text{int}}$	0.037
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.019, 0.047, 1.03
No. of reflections	3784
No. of parameters	158
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $e \text{ \AA}^{-3}$ )	0.49, $-0.38$

Computer programs: *APEX* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL2017* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

### Synthesis and crystallization

A mixture of phenylhydrazine hydrochloride (5.56 mmol), 3-methylbutan-2-one (6.67 mmol),  $\text{H}_2\text{SO}_4$  (9.36 mmol) and 20 ml of a solution of acetone-ethanol (1:1 v/v) was refluxed under stirring for 4 h (Fig. 3). The progress of the reaction was monitored by thin-layer chromatography (TLC). The solvent was partially evaporated and the pH adjusted to 4. The organic layer was separated from the aqueous phase by liquid-liquid extraction with dichloromethane ( $3 \times 30$  ml). The organic layer was dried with  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. It is worth mentioning that it was necessary to perform a salting-out step for the separation of the layers. No additional treatments were performed for the indole quaternization step. The indole quaternization was afforded by addition of indole (1.9 mmol) to an excess of iodobutane (9.9 mmol) in acetonitrile, previously saturated with  $\text{N}_2$ . The reaction was conducted under reflux temperature and stirring under a nitrogen atmosphere for 18 h. The reaction was monitored by TLC. The reaction crude was poured into ethyl acetate (50 ml) and allowed to stir under heating for 30 min. Thereafter, the supernatant was removed and the process was repeated three



**Figure 3**  
Synthesis scheme for the title compound.

times. The resulting solid was filtered off and dried (yield 70%). The crystallization was performed with addition of methanol to dissolve the solid followed by the addition of ethyl acetate (m.p. 490 K).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (ppm) 7.65 (*m*, 1H), 7.56 (*m*, 3H), 4.65 (*t*, 2H,  $J = 8.0$  Hz), 3.10 (*s*, 3H), 1.91 (*m*, 2H), 1.63 (*s*, 6H), 1.49 (*m*, 2H), 0.98 (*t*, 3H,  $J = 8.0$  Hz).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 300 MHz):  $\delta$  (ppm) 7.74 (*m*, 1H), 7.61 (*m*, 1H), 4.67 (*t*, 2H,  $J = 7.5$  Hz), 3.13 (*s*, 3H), 1.96 (*m*, 2H), 1.67 (*s*, 6H), 1.53 (*m*, 2H), 1.01 (*t*, 3H,  $J = 6.0$  Hz)  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 75 MHz):  $\delta$  (ppm) 195.5, 141.5, 140.7, 130.0, 129.4, 123.4, 115.3, 54.6, 49.7, 29.8, 23.1, 20.0, 17.0, 13.6.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms were refined as riding on their attached C atoms; the methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The constraint  $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$ , with  $k = 1.2$  for CH and  $\text{CH}_2$  groups and  $k = 1.5$  for methyl groups was applied.

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## full crystallographic data

*IUCrData* (2018). 3, x181130 [https://doi.org/10.1107/S2414314618011306]

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## 1-Butyl-2,3,3-trimethylindol-1-ium iodide

*Crystal data*

$C_{15}H_{22}N^+I^-$

$M_r = 343.23$

Orthorhombic, *Pbca*

$a = 15.631$  (12) Å

$b = 11.614$  (8) Å

$c = 16.976$  (11) Å

$V = 3082$  (4) Å<sup>3</sup>

$Z = 8$

$F(000) = 1376$

$D_x = 1.480$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9006 reflections

$\theta = 2.6$ – $28.2^\circ$

$\mu = 2.06$  mm<sup>-1</sup>

$T = 150$  K

Needle, light brown

$0.37 \times 0.10 \times 0.09$  mm

*Data collection*

Bruker APEX CCD detector  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2015)

$T_{\min} = 0.637$ ,  $T_{\max} = 0.746$

41973 measured reflections

3784 independent reflections

3166 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 28.3^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -8 \rightarrow 20$

$k = -15 \rightarrow 15$

$l = -22 \rightarrow 22$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.019$

$wR(F^2) = 0.047$

$S = 1.03$

3784 reflections

158 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2 + 1.6747P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.49$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.37$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.30279 (12)	0.35676 (13)	0.65813 (9)	0.0198 (3)
C2	0.21170 (11)	0.31229 (14)	0.65947 (9)	0.0199 (3)
C3	0.21293 (11)	0.23111 (13)	0.59009 (9)	0.0179 (3)
C4	0.29095 (10)	0.24303 (13)	0.55103 (9)	0.0165 (3)
C5	0.31022 (11)	0.18740 (14)	0.48120 (9)	0.0201 (3)
H5	0.362745	0.199361	0.454265	0.024*
C6	0.24721 (12)	0.11220 (14)	0.45275 (9)	0.0222 (4)
H6	0.257625	0.070940	0.405389	0.027*
C7	0.16967 (12)	0.09619 (14)	0.49194 (10)	0.0229 (4)
H7	0.129118	0.043056	0.471549	0.028*
C8	0.15075 (11)	0.15720 (15)	0.56079 (10)	0.0218 (3)
H8	0.097231	0.148388	0.586626	0.026*
C9	0.18792 (12)	0.25620 (17)	0.73851 (10)	0.0286 (4)
H9A	0.230985	0.198271	0.752297	0.043*
H9B	0.131775	0.219254	0.733967	0.043*
H9C	0.185859	0.315308	0.779666	0.043*
C10	0.15024 (14)	0.41470 (17)	0.64136 (12)	0.0337 (4)
H10A	0.154360	0.472001	0.683564	0.050*
H10B	0.091326	0.386260	0.637986	0.050*
H10C	0.166415	0.450183	0.591146	0.050*
C11	0.34125 (13)	0.42907 (15)	0.72083 (10)	0.0280 (4)
H11A	0.365790	0.379431	0.761679	0.042*
H11B	0.297002	0.478211	0.744126	0.042*
H11C	0.386361	0.477354	0.698117	0.042*
C12	0.43452 (11)	0.34915 (14)	0.57497 (10)	0.0204 (3)
H12A	0.447583	0.428413	0.592736	0.024*
H12B	0.440974	0.346896	0.516979	0.024*
C13	0.49862 (11)	0.26586 (14)	0.61218 (10)	0.0213 (3)
H13A	0.556043	0.301760	0.610894	0.026*
H13B	0.482947	0.254517	0.668152	0.026*
C14	0.50385 (13)	0.14869 (16)	0.57259 (11)	0.0285 (4)
H14A	0.516312	0.159241	0.515870	0.034*
H14B	0.447852	0.109433	0.577200	0.034*
C15	0.57325 (15)	0.0730 (2)	0.60951 (15)	0.0459 (6)
H15A	0.574132	-0.002022	0.583103	0.069*
H15B	0.561002	0.062175	0.665637	0.069*
H15C	0.629065	0.110399	0.603421	0.069*
N1	0.34412 (9)	0.32083 (11)	0.59593 (8)	0.0172 (3)
I1	0.42439 (2)	0.38097 (2)	0.32579 (2)	0.02455 (4)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0245 (9)	0.0142 (7)	0.0206 (7)	0.0005 (7)	0.0002 (7)	0.0011 (6)
C2	0.0207 (8)	0.0199 (7)	0.0190 (7)	0.0025 (7)	0.0021 (7)	-0.0027 (6)

C3	0.0187 (8)	0.0179 (7)	0.0171 (7)	0.0019 (6)	-0.0002 (6)	0.0010 (6)
C4	0.0167 (8)	0.0145 (7)	0.0183 (7)	0.0003 (6)	-0.0029 (6)	0.0008 (5)
C5	0.0209 (8)	0.0220 (8)	0.0175 (7)	0.0011 (7)	0.0021 (7)	0.0009 (6)
C6	0.0275 (9)	0.0223 (8)	0.0168 (7)	0.0034 (7)	-0.0052 (7)	-0.0024 (6)
C7	0.0234 (9)	0.0214 (8)	0.0240 (8)	-0.0029 (7)	-0.0080 (7)	-0.0002 (6)
C8	0.0166 (8)	0.0256 (8)	0.0231 (8)	-0.0009 (7)	-0.0012 (7)	0.0017 (6)
C9	0.0289 (10)	0.0345 (9)	0.0223 (8)	-0.0065 (8)	0.0055 (8)	-0.0006 (7)
C10	0.0342 (11)	0.0331 (9)	0.0337 (10)	0.0159 (9)	-0.0002 (9)	-0.0058 (8)
C11	0.0369 (11)	0.0229 (8)	0.0242 (8)	-0.0073 (8)	0.0005 (8)	-0.0061 (7)
C12	0.0190 (8)	0.0192 (7)	0.0229 (8)	-0.0051 (7)	0.0015 (7)	0.0021 (6)
C13	0.0180 (8)	0.0243 (8)	0.0216 (8)	-0.0032 (7)	0.0010 (7)	0.0017 (6)
C14	0.0268 (10)	0.0278 (8)	0.0309 (9)	0.0041 (8)	-0.0046 (8)	-0.0028 (7)
C15	0.0403 (13)	0.0395 (12)	0.0580 (14)	0.0189 (11)	-0.0151 (11)	-0.0138 (10)
N1	0.0183 (7)	0.0146 (6)	0.0186 (6)	-0.0018 (5)	-0.0004 (6)	-0.0001 (5)
I1	0.02565 (7)	0.02731 (7)	0.02070 (6)	-0.00322 (5)	0.00032 (5)	-0.00084 (4)

*Geometric parameters (Å, °)*

C1—C2	1.515 (3)	C10—H10A	0.9800
C1—C11	1.483 (2)	C10—H10B	0.9800
C1—N1	1.306 (2)	C10—H10C	0.9800
C2—C3	1.509 (2)	C11—H11A	0.9800
C2—C9	1.537 (2)	C11—H11B	0.9800
C2—C10	1.560 (3)	C11—H11C	0.9800
C3—C4	1.395 (2)	C12—H12A	0.9900
C3—C8	1.389 (2)	C12—H12B	0.9900
C4—C5	1.383 (2)	C12—C13	1.529 (2)
C4—N1	1.445 (2)	C12—N1	1.494 (2)
C5—H5	0.9500	C13—H13A	0.9900
C5—C6	1.402 (2)	C13—H13B	0.9900
C6—H6	0.9500	C13—C14	1.520 (2)
C6—C7	1.395 (3)	C14—H14A	0.9900
C7—H7	0.9500	C14—H14B	0.9900
C7—C8	1.398 (2)	C14—C15	1.530 (3)
C8—H8	0.9500	C15—H15A	0.9800
C9—H9A	0.9800	C15—H15B	0.9800
C9—H9B	0.9800	C15—H15C	0.9800
C9—H9C	0.9800		
C11—C1—C2	124.28 (15)	H10A—C10—H10B	109.5
N1—C1—C2	111.60 (14)	H10A—C10—H10C	109.5
N1—C1—C11	124.09 (17)	H10B—C10—H10C	109.5
C1—C2—C9	112.64 (14)	C1—C11—H11A	109.5
C1—C2—C10	108.42 (15)	C1—C11—H11B	109.5
C3—C2—C1	100.91 (13)	C1—C11—H11C	109.5
C3—C2—C9	114.81 (15)	H11A—C11—H11B	109.5
C3—C2—C10	109.30 (14)	H11A—C11—H11C	109.5
C9—C2—C10	110.27 (15)	H11B—C11—H11C	109.5

C4—C3—C2	108.68 (14)	H12A—C12—H12B	107.8
C8—C3—C2	131.06 (16)	C13—C12—H12A	109.1
C8—C3—C4	120.19 (15)	C13—C12—H12B	109.1
C3—C4—N1	108.31 (14)	N1—C12—H12A	109.1
C5—C4—C3	123.46 (15)	N1—C12—H12B	109.1
C5—C4—N1	128.23 (15)	N1—C12—C13	112.46 (14)
C4—C5—H5	122.2	C12—C13—H13A	108.6
C4—C5—C6	115.67 (16)	C12—C13—H13B	108.6
C6—C5—H5	122.2	H13A—C13—H13B	107.6
C5—C6—H6	119.0	C14—C13—C12	114.77 (14)
C7—C6—C5	121.94 (16)	C14—C13—H13A	108.6
C7—C6—H6	119.0	C14—C13—H13B	108.6
C6—C7—H7	119.5	C13—C14—H14A	109.3
C6—C7—C8	120.99 (16)	C13—C14—H14B	109.3
C8—C7—H7	119.5	C13—C14—C15	111.80 (16)
C3—C8—C7	117.67 (16)	H14A—C14—H14B	107.9
C3—C8—H8	121.2	C15—C14—H14A	109.3
C7—C8—H8	121.2	C15—C14—H14B	109.3
C2—C9—H9A	109.5	C14—C15—H15A	109.5
C2—C9—H9B	109.5	C14—C15—H15B	109.5
C2—C9—H9C	109.5	C14—C15—H15C	109.5
H9A—C9—H9B	109.5	H15A—C15—H15B	109.5
H9A—C9—H9C	109.5	H15A—C15—H15C	109.5
H9B—C9—H9C	109.5	H15B—C15—H15C	109.5
C2—C10—H10A	109.5	C1—N1—C4	109.97 (14)
C2—C10—H10B	109.5	C1—N1—C12	126.15 (14)
C2—C10—H10C	109.5	C4—N1—C12	123.79 (13)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C5—H5...I1	0.95	3.18	3.899 (2)	134
C12—H12 <i>A</i> ...I1 <sup>i</sup>	0.99	3.29	4.186 (3)	151
C12—H12 <i>B</i> ...I1	0.99	3.28	4.249 (3)	167
C13—H13 <i>B</i> ...I1 <sup>ii</sup>	0.99	3.24	4.172 (3)	158

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x, -y+1/2, z+1/2$ .